New Contact Insecticides from Fatty Alcohols

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THE present development is the outcome of a broad investigation of new contact insecticides carried out at the du Pont Experimental Station for the Grasselli Chemical Company with the object of producing a synthetic organic product superior to the plant extractives now used with respect to efficiency, safety, and availability of raw materials.

Early in this work it was found that the higher fatty alcohols typified by lauryl alcohol possessed high insecticidal action against aphids and, furthermore, were free from the disadvantage of the corresponding fatty acids in reacting with the constituents of hard water. Encouraged by these results, numerous long-chain alkyl derivatives were synthesized and tested. Particularly effective compounds were found in the rhodanates of the higher fatty alcohols (*3*) and these have proved to be the most satisfactory from the standpoint of efficiency, safety to foliage, and practicability. The present paper outlines briefly the chemistry of these compounds and deals more specifically with the striking relationship which has been found to exist between molecular weight and toxicity and which has been used as the basis for selecting the most satisfactory product.

The chemical reactions involved in the preparation of long-chain rhodanates are: (1) reduction of natural glycerides to the corresponding long-chain alcohols, (2) conversion of the alcohols to chlorides by means of hydrogen chloride, and (3) preparation of the rhodanates by reacting the chlorides with sodium rhodanate. These reactions are given in the following equations using the synthesis of lauryl rhodanate from trilaurin as a typical example (*2*):

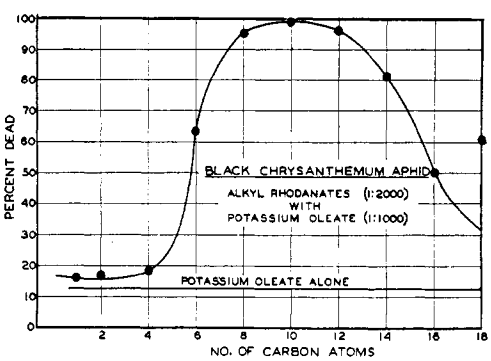

FIGURE 1. RELATIVE EFFICIENCY OF ALKYL RHODANATES AGAINST BLACK CHRYSANTHEMUM APHID

$$\begin{array}{l} CH_3(CH_2)_{10}COO \cdot CH_2 \\ CH_3(CH_2)_{10}COO \cdot CH \\ CH_3(CH_2)_{10}COO \cdot CH_2 \end{array} + 6H_2 \longrightarrow 3CH_3(CH_2)_{10}CH_2OH + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} \quad (1)$$

$$CH_3(CH_2)_{10}CH_2OH + HCl \longrightarrow CH_3(CH_2)_{10}CH_2Cl + H_2O \quad (2)$$

$$CH_3(CH_2)_{10}CH_2Cl + NaSCN \longrightarrow CH_3(CH_2)_{10}CH_2SCN + NaCl \quad (3)$$

By starting with coconut oil as the natural glyceride, it is possible to obtain in this way all of the even-carbon rhodanates from the six-carbon to the eighteen-carbon product. These include hexyl, octyl, decyl, lauryl, myristyl, cetyl, and stearyl rhodanates. Hexyl rhodanate is a mobile liquid boiling at 85° C. under 5-mm. pressure, whereas stearyl rhodanate is a waxy solid boiling at about 195° C. under 2-mm. pressure. Whereas the lower rhodanates up to the hexyl compound have powerful and objectionable odors, this property is considerably reduced in the longer chain compounds, and highly purified lauryl rhodanate has a mild and fatty odor.

Relation of Insecticidal Action to Molecular Weight

For the purpose of investigating in detail the relationship of the contact insecticidal action of these rhodanates to their molecular weight, the writers have supplemented the series of rhodanates obtainable from coconut oil with the lower rhodanates, including the methyl, ethyl, and butyl derivatives. A few tests on the less readily accessible nonyl and undecyl rhodanates have indicated that these odd-carbon products follow the toxicity trend established by the even-carbon homologs. Representative branched-chain rhodanates have also been included in the tests; but since these, on the whole, have given less promising results, the discussion in this paper will be limited to the normal primary compounds in which there is a straight chain of carbon atoms with a terminal rhodanate group. The results of tests in the greenhouse and laboratory on black chrysanthemum aphids, green chrysanthemum aphids,

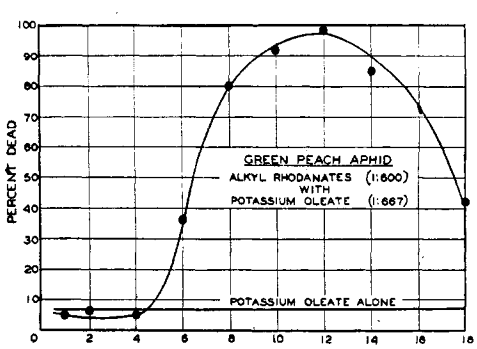

FIGURE 2. RELATIVE EFFICIENCY OF ALKYL RHODANATES AGAINST GREEN PEACH APHID

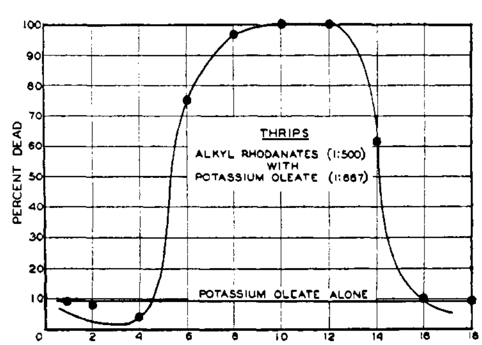

FIGURE 3. RELATIVE EFFICIENCY OF ALKYL RHODANATES AGAINST THRIPS

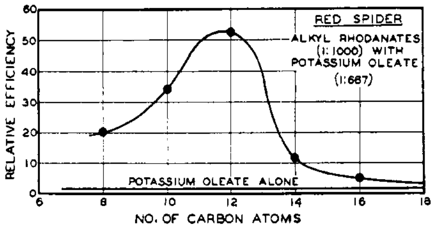

FIGURE 4. RELATIVE EFFICIENCY OF ALKYL RHODANATES AGAINST RED SPIDER

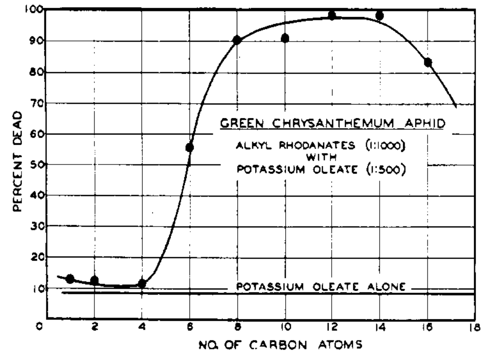

FIGURE 5. RELATIVE EFFICIENCY OF ALKYL RHODANATES AGAINST GREEN CHRYSANTHEMUM APHID

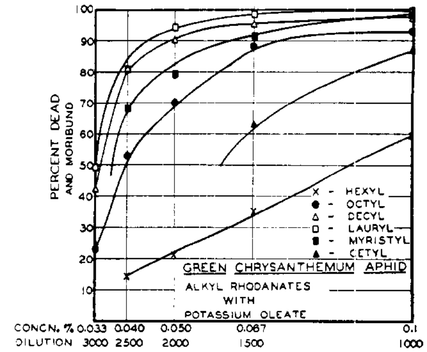

FIGURE 6. CONCENTRATION-CONTROL CURVES FOR ALKYL RHODANATES AGAINST GREEN CHRYSANTHEMUM APHID

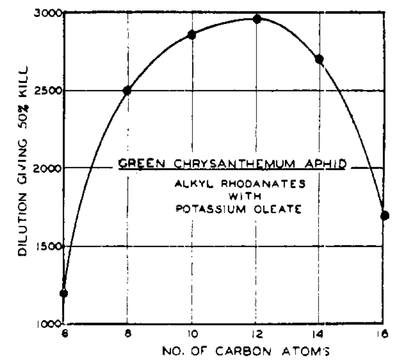

FIGURE 7. DILUTION OF ALKYL RHODANATES REQUIRED FOR 50 PER CENT KILL OF GREEN CHRYSANTHEMUM APHID

thrips, green peach aphids, and red spiders are presented graphically. In these tests a chemically pure and reproducible spreader was used—namely, potassium oleate—and the concentrations of the rhodanates and the spreader were chosen sufficiently low so as to bring out clearly the differences between the efficiencies of the homologous members of the series. For this reason the results presented below are to be considered as relative rather than indicative of control under optimum conditions.

Biological Test Methods

Several methods, depending on the availability and habits of the test species, were used in evaluating the relative efficiency of the homologs of lauryl rhodanate. These methods have been described and designated by Peterson (*1*) as the "embroidery hoop, plate, and potted plant methods." All homologs were tested on a given species simultaneously and in the same experimental series to eliminate the influence of variable external conditions. In each series three replications or tests of each homolog were employed, and the average of the results obtained from these were used as the measure of the relative efficiency of each homolog. The number of individuals used varied with the test species. The average number of individuals in the case of the several species of aphids was two hundred in each replication. The average number of red spiders in each replication was likewise two hundred. It has been repeatedly observed that the immature stages of thrips were more susceptible to contact insecticides than the adults. Therefore, in taking data the stages were counted separately, but only the data relating to the adults have been used. The adults were very active and not gregarious so that the average number in each replication was low—forty-five. Such deficiency in numbers was compensated for by repeating the test series so that a total of sixteen replications for each homolog was used. All materials were applied with an atomizer type sprayer, operating under constant air pressure. Counts of live, dead, and moribund individuals were always made under a broad-field binocular microscope in order to determine more accurately the moribund class.

Discussion of Results

In Figure 1 the percentage kill obtained with black chrysanthemum aphids is shown with the rhodanates used at a concentration of 1 to 2000 and potassium oleate at a concentration of 1 to 1000. The kills obtained with the methyl, ethyl, and butyl compounds are hardly greater than those with potassium oleate alone, but with the six-carbon product there is a definite rise in toxicity which reaches a peak with the octyl, decyl, and lauryl rhodanates and then falls off rapidly with the myristyl and cetyl derivatives. The eighteen-carbon point is in error, partly because of the fact that being a waxy solid it demanded the use of a higher concentration of potassium oleate. The results on green peach aphids shown in Figure 2 reveal a definite peak at the twelve-carbon product. As might be expected, the differentiation between the homologs is augmented in the case of the most resistant species of insects. Figure 3 shows that the maximum efficiency against thrips is reached at the ten- and twelve-carbon products. In Figure 4 we have a curve on red spider in which the alkyl rhodanates are used at a concentration of 1 to 1000. The lauryl compound is outstandingly superior to the other homologs against this mite.

In Figure 5 the percentage kill of green chrysanthemum aphids is shown for the rhodanates at a concentration of 1 to 1000 and the potassium oleate at 1 to 500. The efficiency rises from practically zero for the lower homologs to 95–100 per cent for lauryl rhodanate, a marked decrease appearing again with the sixteen-carbon product. A more reliable indication of relative toxicity can be obtained by comparing the rhodanates at several concentrations and drawing concentration-control curves as shown in Figure 6. From these curves it is possible to determine the concentration of each homolog required to give 50 per cent dead and moribund; these figures have been plotted against molecular weight in Figure 7. The peak in efficiency occurs at the twelve-carbon product, lauryl rhodanate giving 50 per cent dead and moribund at a dilution of about 1 to 3000.

The unusually high efficiency of lauryl rhodanate can probably be explained on the basis of favorable physical properties leading to good spreading and penetrating characteristics. At the present time, however, no one physical property has been found to correlate with this peak in the toxic action, and it seems unlikely that such a property will be found but that instead the peak at twelve-carbon atoms is reached through the resultant of several properties. The usual physical properties which have been used to explain toxicity are found either to increase or decrease progressively with molecular weight without showing a maximum or minimum. For example, determination of the surface tensions of the rhodanates has shown that this property increases progressively with increase in molecular weight in the range from eight to sixteen carbon atoms. The solubilities in water and vapor pressure curves have not been determined quantitatively, but these properties certainly decrease with increase in molecular weight. All of these factors would be expected to have some effect on the penetration of these compounds from aqueous emulsions into the insects and apparently reach a most favorable balance with the twelve-carbon product.

Plant Tolerance Tests

Because the twelve-carbon homolog has shown a high relative efficiency, this product was selected for extensive plant tolerance tests. Numerous combinations of both the pure and commercial product in various dispersing agents have been used in laboratory, greenhouse, and field tests. At effective concentrations and in the proper dispersing medium, a sufficiently wide margin of safety to many kinds of plants has been found to warrant the use of such combinations as commercial insecticides.

Acknowledgment

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Literature Cited

(1) Peterson, Manual of Entomological Equipment and Methods, Part 1, plate 127, No. 2, 4-6, Edwards Bros., 1934.
(2) Salzberg and Bousquet, U. S. Patent 1,963,100 (June 19, 1934).
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Prevention of Gas Explosions by Controlling Oxygen Concentration

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An investigation of the values below which the oxygen must be maintained to prevent explosions of combustible gases and vapors is described. The respective critical oxygen values obtained when carbon dioxide or nitrogen is used as the inert diluent are as follows for the various gases investigated: methane, 14.6 and 12.1; ethane, 13.4 and 11.0; propane, 14.3 and 11.4; butane, 14.5 and 12.1; pentane, 14.4 and 12.1; hexane, 14.5 and 11.9; ethylene, 11.7 and 10.0; propylene, 14.1 and 11.9; hydrogen, 5.9 and 5.0; and carbon monoxide, 5.9 and 5.6 per cent by volume.

Elevated temperatures cause a widening of the inflammable limits of combustible gases and vapors and therefore a decrease in the oxygen concentration necessary to prevent flame propagation. The values given in this report hold only for temperatures below 40° C. and for ordinary variations of atmospheric pressure.

EXPLOSIVE mixtures of combustible gases and vapors may be rendered nonexplosive by reducing the oxygen concentration below certain critical values. This is of special importance in the repair of equipment, such as gas lines, tank cars, and gas holders which contain combustible gases or vapors. The operations may be carried out with safety, provided the kind and proportions of combustibles present are known and the oxygen is kept below the amount required to propagate flames of these combustibles.

The Bureau of Mines has been obtaining data whereby the explosive or inflammable limits of complex combustible gas mixtures, such as mine-fire gases, gases produced during mine explosions, and natural gases containing high percentages of carbon dioxide and nitrogen, may be determined by calculation (*2*, *4*). These investigations have given information on the oxygen percentages required to prevent explosions of many of the commonly occurring combustible gases and vapors.

Various methods have been used to determine the oxygen values below which explosive mixtures are rendered nonexplosive. Rhead (*7*) and others (*6*, *8*) have obtained the oxygen percentage in atmospheres at or below which flames of combustibles were extinguished by burning the combustibles in a closed chamber. As the gas burned in the closed space, the oxygen was consumed by the combustion process. Eventually a time was reached when the oxygen supply became sufficiently reduced to extinguish the flame. Analysis of samples of the atmosphere taken at the time the flame was extinguished gave the amount of oxygen present. The values obtained by this "residual atmosphere" method have been found to vary with the design of the burner, with the rate at which the gas is burned, and with the amount of primary air introduced into the gas before burning.

Table I gives the values obtained by investigators using the residual atmosphere method and, for comparison, values obtained by the explosion tube method used during the investigation described in this paper. The extent to which the values may vary by the residual atmosphere method is apparent from the data given for natural gas. When natural gas heaters were allowed to burn in a 1000-cubic foot sealed chamber, and the atmosphere was sampled and analyzed at the time the flames were extinguished, the results showed that the critical oxygen values depended on the type of heater used